

Chemical sensing based on the plasmonic response of nanoparticle aggregation: Anion sensing in nanoparticles stabilized by amino-functional ionic liquid

Aitzol GARCIA-ETXARRI^{1,2}, Javier AIZPURUA^{1,2,*}, Jon MOLINA-ALDAREGUIA^{3,4},
Rebeca MARCILLA⁵, Jose Adolfo POMPOSO^{5,1}, David MECERREYES^{5,†}

¹Donostia International Physics Center DIPC, Paseo Manuel de Lardizabal 4, 20018 Donostia-San Sebastián, Spain

²Centro de Física de Materiales, Centro Mixto CSIC-UPV/EHU, Centro Kortza, Avenida de Tolosa 72,
20018 Donostia-San Sebastián, Spain

³CEIT–Centro de Estudios e Investigaciones Técnicas de Gipuzkoa, Paseo Manuel de Lardizabal 15,
20018 Donostia-San Sebastian, Spain

⁴IMDEA Materials, E. T. S. de Ingenieros de Caminos, c/Profesor Aranguren, s/n, 28040 Madrid, Spain

⁵CIDETEC–Centre for Electrochemical Technologies, Parque Tecnológico de San Sebastian,
Paseo Miramon 196, 20009 Donostia-San Sebastian, Spain
E-mail: *aizpurua@ehu.es, †dmecerreyes@cidetec.es

Received December 30, 2009; accepted January 25, 2010

We report the synthesis, characterization and modellization of optical anion sensors based on gold nanoparticles (Au NPs) stabilized by amino-functional imidazolium ionic liquids (AFIL). The addition of different salts results in anion exchange of the imidazolium ionic liquid stabilizer leading to a change in the optical response of the original nanoparticle aqueous solution. In all cases except with dodecylbenzenesulfonic acid sodium salt, a sufficient amount of salt concentration (5 times larger than equimolar) leads to the appearance of an absorption band between 600 and 700 nm in the ultraviolet-visible (UV-vis) spectrum. The presence of the salt produces aggregation of the particles that localise the optical response and produce a large spectral red shift. Transmission electron microscopy images demonstrated that this optical change was due to the aggregation of the nanoparticles. We simulate the optical response of both situations, before and after salt addition, and interpret the experimental observations in terms of the different response of metallic single nanoparticles and nanoparticle aggregates. Theoretical calculations for single nanoparticle and single nanoparticle dimers demonstrate that the colour change is not due to the enlargement or structural changes of the Au NPs, but due to the formation of NP aggregation. These results show the potential of nanoparticle plasmonics to perform effective chemical sensing.

Keywords ionic liquids, metallic nanoparticles, surface plasmons, anion sensor

PACS numbers 73.20.Mf, 78.30.cd, 82.33.Hk

1 Introduction

Metallic nanoparticles have been intensively used as nanoscale sensors and actuators in many different fields such as optics, chemistry, or biology due to the high sensitivity of their optical response to changes in the surrounding media. The optical response in metals is governed by absorption and scattering of light at certain resonant wavelengths associated with the excitation of surface plasmons. Originally, the use of surface plasmon polaritons (SPP) for sensing purposes was first developed in the context of total attenuated reflection measurements

in metallic layers [1]. A variety of samples, from gases [2] to antigen-antibody complexes [3], have been addressed and detected with use of variations of this technique. The use of metallic nanoparticles and structures with complex geometries exciting localised surface plasmons (LSP) triggered out a race for understanding the plasmon shifts as a function of size, shape, and composition of the nanostructures involved [4, 5]. The versatility of chemical and lithographic methods to create a variety of nanostructures has sophisticated the catalogue of particles and structures currently available for spectroscopy [6], microscopy [7], and sensing [8].

The optical properties of gold nanoparticles, conve-

niently functionalized, have been the basis of many detectors and sensing schemes. For example, in chemistry, functionalized metallic nanoshells have been proved to act as a PH sensor [9], or in biology, oligonucleotide-modified nanoparticle aggregates [10] have been implemented as polynucleotide detectors based on the distance-dependent optical properties of the nanoparticles. Even specificity in detection of nucleotide defects, such as the presence of missing or extra nucleotides in DNA chains, has been reported [11] with use of a particle dimer scheme, and more recently, gene manipulation has been achieved with use of these nanoparticles [12]. Due to these successful applications, nanoparticle plasmonics has experienced some of the most promising developments in fields like chemistry, biology, gene detection and specificity.

In this work, we focus on the synthesis and application of a new type of gold nanoparticles, stabilized by amino-functionalized ionic liquid bearing an imidazolium group. These novel particles present anion sensing capabilities due to the response of the nanoparticle aggregation to the addition of different salts. Some studies on optical response of aggregates as a function of salt concentration [13, 14] have been developed recently, oriented to understand the melting properties of DNA-linked gold nanoparticles. In our case, the presence of the amine group in the ionic liquid (IL) prevents particle aggregation in the absence of salts in solution, and even in small salt concentration. As the salt concentration is increased in solution, the nanoparticles aggregate, yielding a different optical response, red-shifting considerably the plasmonic response of the system. This is the fundamental of the sensing capability.

Ionic liquids have attracted increasing interest due to their interesting properties and, therefore, numerous applications in fields like “green chemistry” [15–17], electrochemistry [18–22] and more recently, nanotechnology [23]. In a pioneering work, a similar strategy to ours was reported by Chujo *et al.* [24] for the synthesis of Au NPs in water using an IL stabilizer based on the imidazolium cation, indicating the possibilities of these systems as optical anion sensors. In this work, we report the one-phase synthesis of Au NPs using an alternative IL, not functionalized with thiol groups. In this case, an amino-functionalized ionic liquid (AFIL) was used as stabilizer in the synthesis of Au NPs. Since changes in the surrounding medium, by addition of different salts, may affect the stabilization and produce nanoparticle aggregation, the possibilities of this system in the development of anion sensors and in nanoparticle phase transfer were also explored. The understanding of the optical plasmon response of stabilized single particles in solution versus particle aggregates is also presented in the next sections. The theoretical concept underlying the anion sensing capacity is the different plasmonic response of

a single metallic sphere, compared to a metallic dimer [25–29]. To that end, we develop exact electromagnetic calculations of the plasmon response of single metallic spherical particles and dimers of coated gold nanoparticles, and report their different scattering properties connected with the change of color in the solutions after salt addition. A boundary element method (BEM) [30, 31] which has been proven to describe accurately the light scattering of complex-shaped metallic nanosystems [32] will be applied, and the far-field (extinction) spectra and near-field distribution around the nanostructures are calculated. The results presented here will be discussed in terms of the potential of these novel amino-functionalized nanoparticles to act as effective anion sensors.

2 Experimental details

2.1 General methods

All reagents were of the highest purity and purchased from Aldrich and used without purification. Ultraviolet-Visible Spectroscopy (UV-Vis) was performed in a Shimadzu UV-1603 spectrophotometer. Transmission electron microscopy (TEM) analysis of the nanoparticles was performed using a Jeol JEM-2100 microscope operated at 200 KV. The samples for the analysis were prepared by depositing diluted particle solutions onto 400-mesh carbon-coated copper grids and leaving the solvent to dry. The synthesis of 1-(3-aminopropyl)-3-butylimidazolium chloride ([AmPrBuIm][Cl]) consisted of a three-step process: (i) protection of amino group, (ii) quaternization, and (iii) unprotection. The resulting ionic liquid was obtained as a viscous liquid. The details of the synthesis are reported elsewhere [33].

2.2 Synthesis of Au NPs stabilized with [AmPrBuIm][Cl]

A solution of the IL in distilled water (10 mg in 10 mL) was mixed with a solution of HAuCl₄ in distilled water (5 mg dissolved in 10 mL). Under vigorous stirring, an aqueous solution of NaBH₄ (0.5 mg in 10 mL) was added dropwise to the previously described solution. The reaction continues for 30 minutes at room temperature, and the colour of the solution changes progressively from pale yellow to dark red-purple [33].

2.3 Effect of added salts on the stability of Au NPs: Typical procedure for anion exchange

Different amounts of several salts (equimolar to [AmPrBuIm][Cl], 5 times more, 50 times more) were added to an aqueous dispersion of Au NPs stabilized by AFIL (30 mL), and the mixture was stirred at room temperature. The added salts were lithium perchlorate (98%), lithium

tetrafluoroborate (98%), sodium chloride ($\geq 99.5\%$), dodecylbenzenesulfonic acid sodium salt (DBSA) (technical grade), lithium triflate (99.995%) and bistrifluoromethanesulfonimide lithium salt (99.0%). The optical changes were followed by UV-Vis spectroscopy.

3 Results and discussion

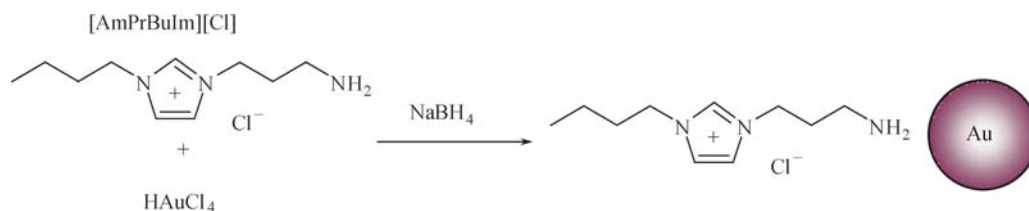
Gold nanoparticles stabilized by an amino-functional imidazolium ionic liquid were synthesized by classical methods using NaBH_4 as reductant [33]. UV-vis spectra of the aqueous colloidal Au NPs dispersion showed a peak with a maximum at 523 nm. Average-size particle and distribution and shape of the Au NPs were determined by Transmission Electron Microscope. The overall analysis shows that AFIL stabilized Au NPs to a small (average diameter (A_v) = 17 nm) size and uniform (standard deviation (SD) = 7 nm).

In a previous communication, Chujo *et al.* [24] reported that gold nanoparticles with a surface modified with thiol functional IL can be used as exceptionally high extinction dyes for colorimetric sensing of anions in water via a particle aggregation process. In fact, the addition of different salts to the thiol functional IL resulted in the anion exchange. Due to this anion exchange, the particles interact differently with each other, aggregating and modifying the surface plasmon absorbance and, consequently, the colour of the colloidal dispersion. In this work, we revisited the idea of taking advantage of the changing properties of the IL around the nanoparticles, in order to provide a new way to control properties of the surfaces and materials, and use this control for anion sensing. In order to develop this application, the addition of several salts in different concentrations (equimolar to $[\text{AmPrBuIm}][\text{Cl}]$, 5 times more, 50 times more) to the colloidal dispersion was carried out. With all the salts except DBSA, that addition provoked colour changes in the dispersion from initial red-purple to blue [Fig. 2 (c)]. These changes were quantified using UV-vis spectroscopy. In Fig. 1, the UV-vis spectra of the colloidal nanoparticles dispersion after addition of several salts in different concentrations are showed. According to the figures, when the salts were added in an equimolar relation with respect to the AFIL, the change in the spectra was small with a slight broadening of the curve. However, when the salts were added in higher relation,

the spectra changed completely inducing a red shift. For example, when 5 times more of salts (with respect to the moles of AFIL) were added, a new band appeared in the spectra at a higher value of wavelength. With some salts like $\text{CF}_3\text{SO}_3\text{Li}$ and NaCl , this new band was smaller than the initial one (at 525.5 nm) and looked like a shoulder from the first band. With other salts like LiBF_4 , LiClO_4 , and $\text{Li}(\text{CF}_3\text{CF}_2\text{SO}_2)_2\text{N}$, the new band was bigger than the first one and appeared at 627 nm, 610.5 nm, 646 nm and 627.5 nm, respectively. When the salts were added in even higher proportion, 50 times more, the new band appeared more pronounced in all the cases. This red shift can be attributed to the coupled plasmon absorbance of the Au NPs in close contact, produced during the anion exchange process and leading to the formation of nanoparticle aggregates. These aggregations are due to the changes in miscibility of the AFIL in the surface of the nanoparticles. The AFIL exchanges the Cl^- anion with the new anions of the added salts resulting in a new AFIL immiscible with water and provoking particles bringing together. However, this behaviour is also seen in the case of NaCl containing the same chloride anion that bears the initial AFIL. In this case, the aggregation of the nanoparticles would be due to destabilization of the dispersion by the increase in the ionic strength of the solution. In all cases, the optical answer of the solutions evolved with time, and after a short period of time (1–2 hours), the solutions became clear and the nanoparticles deposited at the bottom of the flasks.

It is worth to remark that an exception to this behaviour is the addition of dodecylbenzene sulphonic sodium salt (DBSA) that does not result in colour change or shift in the bands. In fact, the addition of DBSA, a well-known surfactant, provokes an additional stabilization to the nanoparticles due to the chemical structure of this anion.

As a summary of the above UV-vis spectra, we are able to associate the presence of new scattering peaks with an increasing concentration of anions and, therefore, establish a quantitative basis for anion concentration sensing. In all the cases except in DBSA, a concentration larger than 5 times the equimolar concentration was needed to produce a clear change in the absorption spectrum. Some differences are observed between salts, but the overall trends are similar which involves the appearance of a second band at wavelength close to 700 nm. The question is why there is such an optical change



Scheme 1 Synthesis of Au NPs in water using $[\text{AmPrBuIm}][\text{Cl}]$ as the stabilizer.

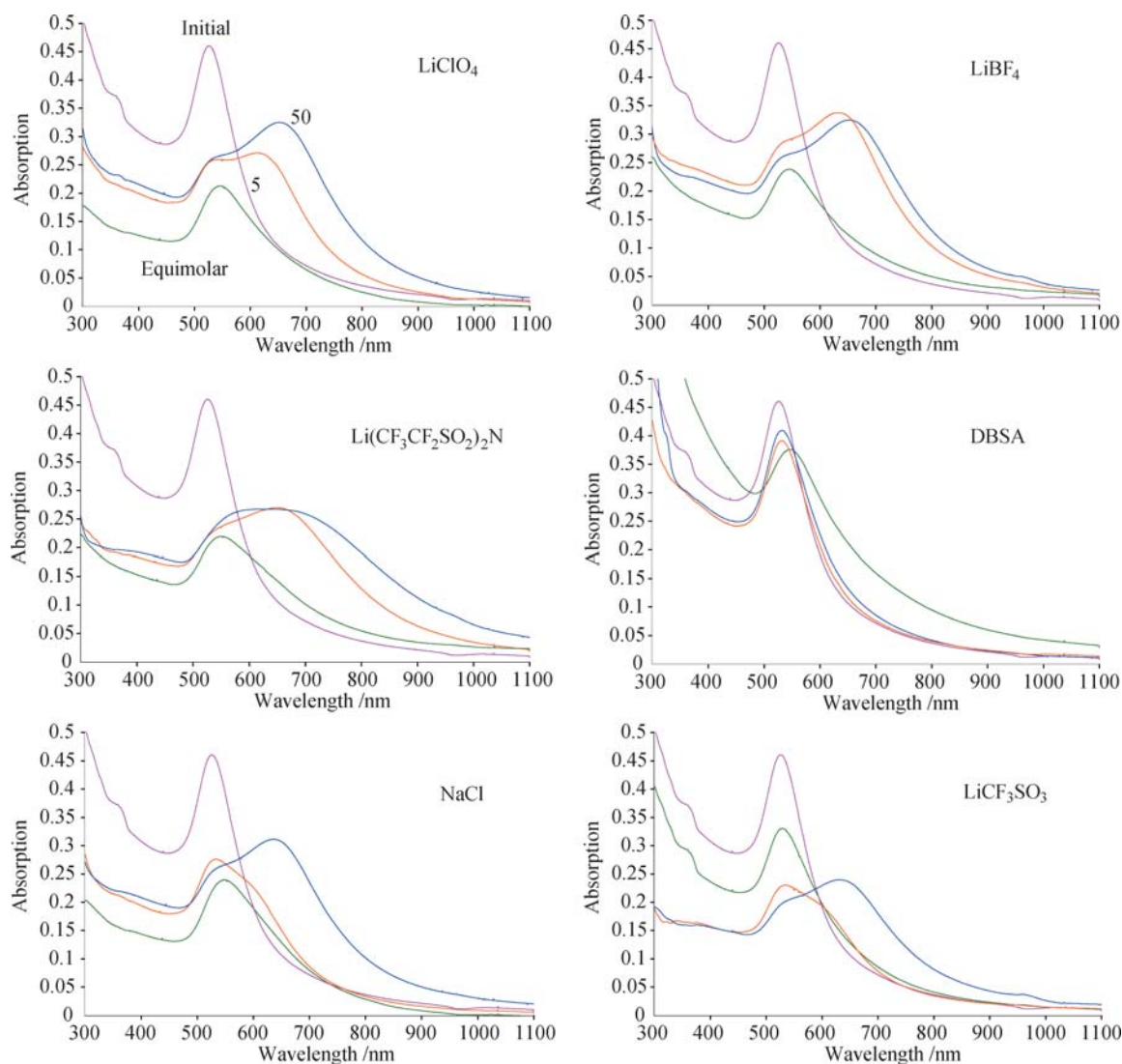


Fig. 1 UV-vis absorption spectra of the nanoparticle solutions before (*pink*) and after addition of several salts (LiClO_4 , LiBF_4 , $\text{Li}(\text{CF}_3\text{CF}_2\text{SO}_2)_2\text{N}$, DBSA, NaCl, LiCF_3SO_3) in different concentrations: equimolar (*green*), 5 times more (*orange*) and 50 times more with respect to the moles of AFIL (*blue*).

in the spectra of the solutions, if it is due to a change in size or shape of the nanoparticles or to an aggregation phenomenon. We tried to answer this question theoretically (see next section) and to find an experimental evidence for this behaviour. For this purpose, we carried out transmission electron microscopy (TEM) analysis of the nanoparticles, as shown in Fig. 2.

Figure 2(a) shows the TEM image corresponding to Au NPs stabilized by amino-functional ionic liquid before any salt was added showing individual nanoparticles. Figure 2(b) shows the TEM image corresponding to the AuNPs solution after addition of LiClO_4 (50 times more) showing a big nanoparticle aggregate induced by the presence of the salt. The photographs of such AuNPs solutions, before and after salt addition, are shown in Fig. 2(c). Similar images were obtained after addition of the other salts.

4 Theoretical basis for plasmon response

We present in this section the theoretical basis for the interpretation of the change of colour of the solutions after the addition of different salts. Metallic nanoparticles are known to absorb visible light at a wavelength that depends strongly on (i) the electronics density of the metals, (ii) the size of the particles, (iii) their shape, (iv) the environment, and (v) the inter-particle interactions. In our case, we deal with gold nanoparticles that present a narrow size dispersion. As observed in the size distribution histogram obtained from our experiments, most of the particles (82%) lie on a diameter range of 5-nm to 25-nm diameter. According to our electromagnetic calculations, this size dispersion in single particles cannot be responsible for a large spectral shift in optical

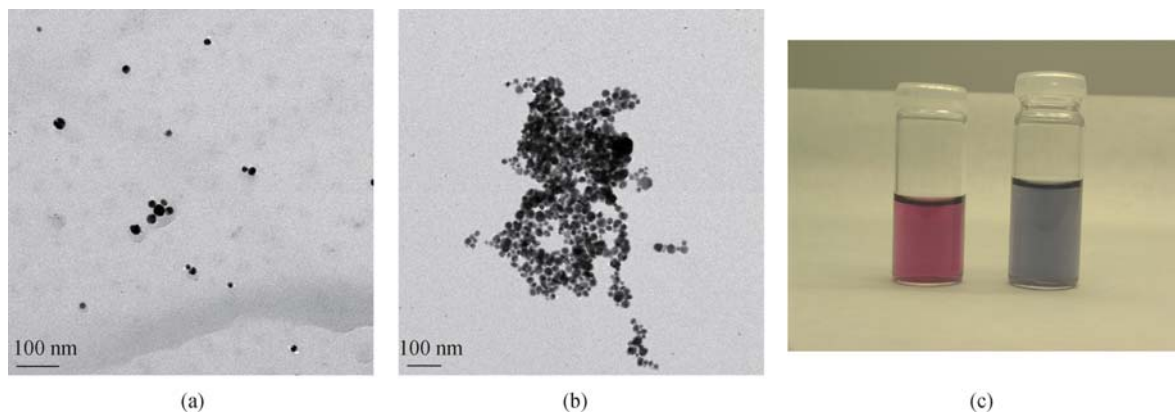


Fig. 2 (a) and (b) TEM images of gold amino-functionalised nanoparticles before (a) and after (b) salt addition (addition of 50 times more in moles of LiClO_4). Single particles in (a) and aggregates of particles in (b) can be clearly distinguished. (c) Photographs of the initial Au NPs solution, before salt addition (*left*) and of the Au NPs solution after addition of 50 times more in moles of LiClO_4 (*right*).

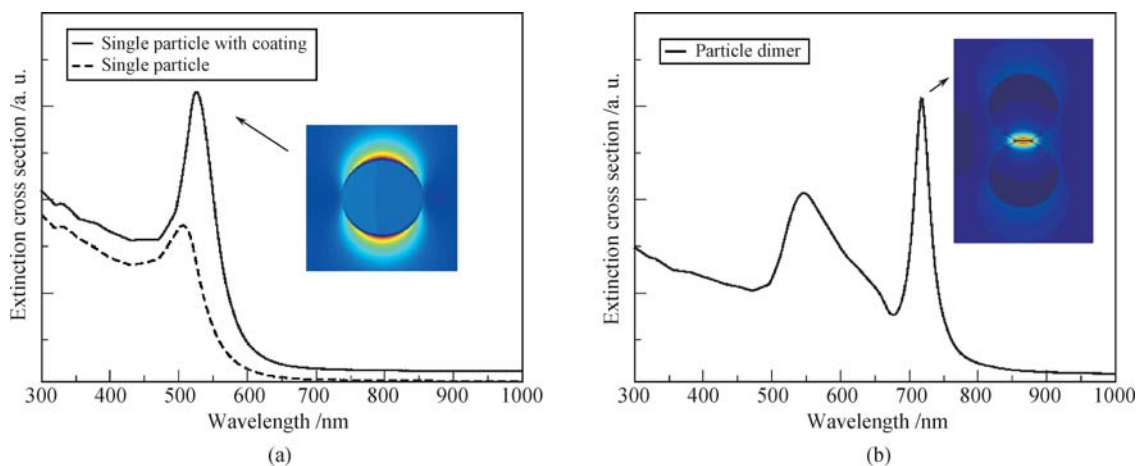


Fig. 3 (a) Theoretical calculation of the extinction cross section (absorption plus scattering) for a 17-nm gold particle with (*solid line*) and without (*dashed line*) a 2-nm coating resembling the polarization of the amino-groups. An effective dielectric constant $\epsilon = 13.5$ is assumed to calculate the effect of the coating. (b) Theoretical calculation of the extinction cross section for a gold dimer of the same size as in (a). Appearance of a red-shifted peak is clear in the spectrum of aggregates. Near-field plots for single particles and aggregates are displayed in the insets at the resonant wavelengths (525 nm and 710 nm, respectively). The red color represents large local field, and the blue color stands for no enhancement.

response. In Fig. 3(a), we plot the extinction spectrum of a single gold nanoparticle of 17 nm. A distinctive extinction peak (*dashed line*) at a wavelength $\lambda=520$ nm can be observed corresponding to the excitation of a dipolar plasmon mode [see inset in Fig. 3(a) with the near-field pattern corresponding to the absorption peak]. A difference in the particle size of a few nanometers only induces a change in plasmon peak position of about 10 nm in wavelength, giving rise to a small inhomogeneous broadening of the optical spectrum due to size dispersion. The shape of the particles also remains spherical during the whole process, discarding plasmon shifts due to geometrical or shape-related issues. To account for polarizability effects of the amino-functional ionic liquid on the particle response [34], we have surrounded the particles with a 2-nm-thick layer of a dielectric material with constant dielectric permittivity $\epsilon=13.5$ (value taken from Ref. [35]). This has a fine-tuning effect in the actual peak position of the single nanoparticle spectrum,

as observed in Fig. 3(a) (*solid line versus dashed line*). The most effective factor changing the optical response of nanoparticles is the interaction with neighbouring particles, as it is the case in particle aggregation. To mimic the situation of particle aggregation, we have performed numerical calculations of the optical extinction spectrum in particle pairs. Values for the particle size and surrounding dielectric environments have been consistent with calculations for the single particle case in (a). The result is displayed in Fig. 3(b), where a new peak ($\lambda=710$ nm) red-shifted with respect to the single particle peak (around 510 nm) is clearly observed. This peak is generated as a consequence of plasmon localisation at the pair junction of the aggregate due to interparticle interaction [25–29]. The local field produced at the junction at $\lambda=710$ nm is reproduced in the inset. These two distinctive ways of optical response for single particle and dimers can be easily traced in absorption spectra.

In Fig. 4, we show the evolution of the extinction spec-

tra as a function of inter-particle separation distance. When the average inter-particle distance is very large, the typical dipolar response is the only feature of the absorption spectrum. As the particle separation decreases, a new peak emerges and red-shifts as the particles become closer. This is the expected behaviour in particle aggregation where the final absorption profile depends on the actual characteristics of the aggregate average separation distance. Depending on the concentration and type of salt added in our solution, one situation (single particle) or the other (aggregates) is created, producing the spectral shift (change of color) shown in Fig. 1 that can be measured experimentally.

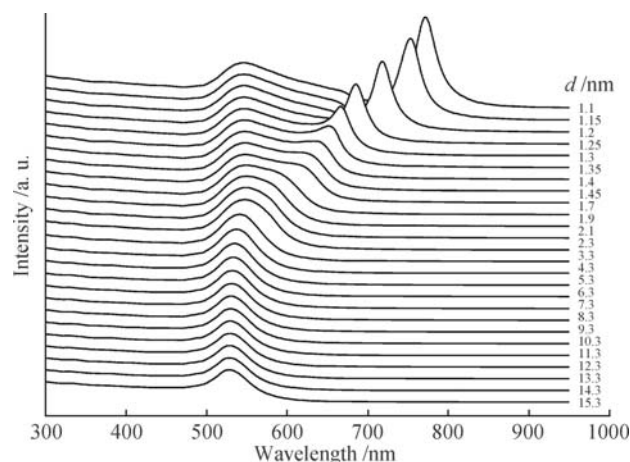


Fig. 4 Extinction cross section (absorption plus scattering) for gold nanoparticle dimers, as a function of separation distance d . The lower part of the graph shows separated particles (single NPs, separation $d=15.3$ nm), whereas the upper side of the graph shows spectra for closely located particles (aggregates separation $d=1.1$ nm).

The theoretical calculations for single nanoparticle and nanoparticle dimers demonstrate that the colour change is not due to the enlargement or structural changes of the Au NPs but due to the formation of NPs aggregation which is in good agreement with the observed nanoparticle aggregates by TEM.

5 Summary and conclusions

In conclusion, gold nanoparticles stabilized by new amino-functional imidazolium ionic liquids were synthesized and investigated as optical anion sensors. The addition of different salts resulted in anion exchange of the imidazolium ionic liquid stabilizer leading to an optical change in the nanoparticle dispersions. According to the experimental observations and theoretical calculations, the optical change of the nanoparticle solutions was due to the aggregation effect of the nanoparticles. The plasmonic response of these novel amino-functionalised nanoparticles opens new opportunities for single nanoparticle stabilization and anion sensing. The

time dependence of the optical response and the similarities between the responses to different anions, which prevents selectivity, are some of the drawbacks of the method that need further improvement and investigation.

Acknowledgements The authors acknowledge financial supports from the Department of Industry of the Government of the Basque Country (Eusko Jaurlaritza) and the Department of innovation of the Diputación Foral de Gipuzkoa through the ETORTEK project NANOTRON and inanoGUNE.

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